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## On elasticity under pressure

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### Abstract

Two recently published ways of calculating the elastic constants for a crystal under hydrostatic pressure are compared. They are shown to be equivalent theoretically, though one is more convenient for numerical simulations. A crystal of ferromagnetic iron in the body-centred cubic structure is used as an example for comparing elastic constants calculated with these two methods.

Interest in the problem of crystal elasticity under pressure has been growing in recent years [1–10]. A non-traditional approach to this problem is proposed in [7]; it uses the Gibbs free energy  $G(P, T) = E(P, T) + PV(P, T)$  instead of the energy  $E$  for estimating elastic constants under pressure  $P$ :

$$\bar{C}_{ij} = \frac{1}{V} \frac{\partial^2 G}{\partial \epsilon_i \partial \epsilon_j} \Big|_{P=\text{const}}. \quad (1)$$

Hereinafter the Voigt notation is used;  $\epsilon_i$  are Eulerian strains. The authors of [7] even argue that ‘the elastic constants are not given by second derivatives of  $E$  with respect to strain’ for systems under pressure. They also state that as long as the equilibrium structure in the system at constant  $P$  and  $T$  is not at a minimum of  $E$ , the use of  $E$  causes difficulties in determining the equilibrium structure at each  $P$ , whereas minimization of  $G$  at fixed  $P$  allows one to avoid difficulties. In the cases of crystals with bct and hcp structures, the authors of [7] suggest the use of the epitaxial Bain path (EBP) to determine the equilibrium structure and calculate the elastic constants from formula (1).

Considering the case of  $T = 0$  in this paper, we note that since strained crystal states are usually non-equilibrium, it is impossible to determine the Gibbs free energy or any other thermodynamic potential at such states. However, the formally introduced function

$$G(P, \epsilon_1, \dots, \epsilon_6) = E(P, \epsilon_1, \dots, \epsilon_6) + PV(P, \epsilon_1, \dots, \epsilon_6), \quad (2)$$

makes the formula for elastic constants under pressure (1) proposed in [7] coincide with the formula derived in [6] from the traditional definition of the elastic constants at  $P = 0$ . The advantage of the approach discussed in [6] lies in the very fact that the formula for the

calculation of the elastic constants under pressure is derived from the traditional definition [11] rather than postulated. We also note that the use of the epitaxial Bain path might cause a number of difficulties in numerical calculations of the elastic constants, while the method of calculation proposed in [6] is more convenient for use in practice. Finally, we will compare the elastic constants under pressure for ferromagnetic iron with the bcc structure (FM bcc Fe) calculated with formulae [6] with those obtained in experiments and those calculated in [7, 8].

We begin with the determination of the equilibrium parameters of the crystal structure. In our opinion, it is significantly simpler to determine equilibrium values of these parameters through the energy  $E$  than through the function (2), since energy in an equilibrium structure is minimum at a constant specific volume  $V$ . And it is much easier to carry out calculations at constant volume than at constant pressure. In particular, having two lattice constants,  $a$  and  $c$ , it is sufficient to determine the equilibrium value for just one parameter,  $\xi = c/a$ , to determine a stable equilibrium structure at the constant volume  $V$ . The pressure corresponding to the equilibrium lattice constants  $a_0(V)$  and  $c_0(V)$  can be easily determined by differentiating energy with respect to volume:

$$P(a_0(V), c_0(V)) = \frac{dE(a_0(V), c_0(V))}{dV}.$$

Now let us consider the calculation of the elastic constants. Equations establishing a relationship between the elastic constants and the energy variation caused by strain at any hydrostatic pressure  $P$  were derived in [6]. It is also shown in [6] that the energy of the strained crystal under hydrostatic pressure  $P$  varies as

$$\Delta E = -P\Delta V + \Delta E_{\text{in}}, \quad (3)$$

where  $\Delta V$  is the volume variation under strain. Formula (29) from [6] can be written as

$$\Delta E_{\text{in}} = \frac{V}{2} \sum_{i,j} \tilde{C}_{ij} \epsilon_i \epsilon_j. \quad (4)$$

Here  $\epsilon_i$  are Eulerian strains, and the values  $\tilde{C}_{ij}$  form a symmetric matrix and depend on the elastic constants  $C_{ij}$ , which are traditionally determined from Lagrangian strains  $\eta_i$  [11]:

$$C_{ij} = \frac{1}{V} \left. \frac{\partial^2 E(V, \{\eta_m\})}{\partial \eta_i \partial \eta_j} \right|_{\{\eta_m=0\}}. \quad (5)$$

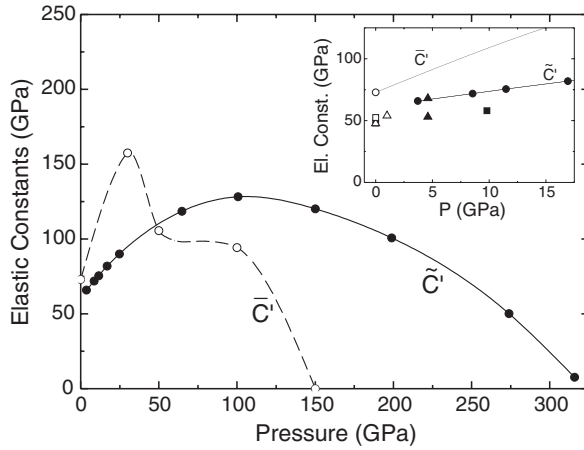
The relationships between  $\tilde{C}_{ij}$  and  $C_{ij}$  are as follows [6]:

$$\begin{aligned} \tilde{C}_{ii} &= \xi_i \xi_j (C_{ii} - P), & i &= 1, 2, \dots, 6; \\ \tilde{C}_{ij} &= \xi_i \xi_j C_{ij}, & i &= 1, 2, 3; & j &= 4, 5, 6; \\ \tilde{C}_{12} &= C_{12} + P, & \tilde{C}_{13} &= C_{13} + P, & \tilde{C}_{23} &= C_{23} + P; \\ \tilde{C}_{45} &= 4C_{45}, & \tilde{C}_{46} &= 4C_{46}, & \tilde{C}_{56} &= 4C_{56}. \end{aligned} \quad (6)$$

Here

$$\xi_i = \begin{cases} 1, & \text{if } i = 1, 2, 3, \\ 2, & \text{if } i = 4, 5, 6. \end{cases}$$

Equality (4), which is valid regardless of whether the strained crystal is in equilibrium or not, allows the authors of [6] to easily generalize the usual Born stability conditions and get the result known from [6]. For cubic structures, relationships (6) between  $\tilde{C}_{ij}$  determining the stability of the crystal under pressure and the elastic constants considered in the traditional definition (5) were derived in [12].

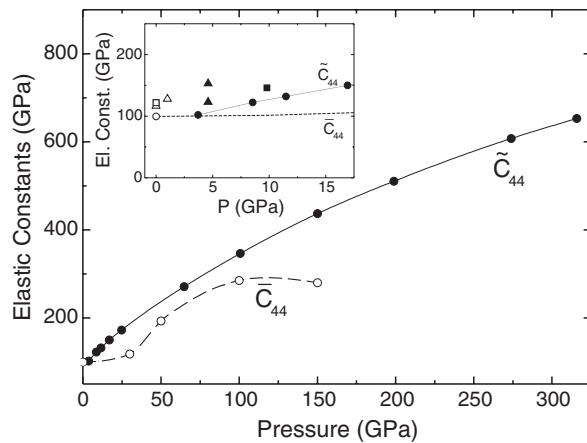


**Figure 1.** The elastic constant  $\tilde{C}'$  for FM bcc Fe as a function of pressure. Solid circles—our results; open circles—results from [7, 8]. Experimental data: solid triangles—[16]; open triangles—[17]; open squares—[18]; solid squares—[19].

Addressing again [7], note that the strain induced change of function (2), which the authors of [7] call the Gibbs free energy, is equal to  $\Delta E_{in}$  as follows from (3). Therefore,  $\bar{C}_{ij}$  (1) axiomatically introduced in [7] will coincide with the values (6) derived in [6] from the traditional definition of the elastic constants [11].

Thus, from the theory standpoint, calculation of the elastic constants under pressure with the method described in [7] will give the same results as the calculation with the method described in [6]. However, in practice it is much more complicated to get the result with method [7] at the same accuracy as with method [6]. For example, if there are two parameters of the crystal lattice,  $c$  and  $a$ , construction of the EBP to determine  $\bar{C}_{ij}$  requires calculation of function (2) in a 2D area surrounding the equilibrium value ( $a_0, c_0$ ). The 2D area cannot be infinitesimally small because of the finite accuracy of the numerical calculation of the strained crystal energy. At the same time, in method [6] it is sufficient to calculate the strained crystal energy as a function of only one variable. This not only reduces the quantity of computations but also simplifies the verification of the calculated results. Our experience shows that if during the calculation of the strained state energy the Fermi surface appears to have different topologies in the equilibrium and strained states, the error of the calculation of the energy derivatives with respect to strain grows significantly. There are more chances for such situations to occur in a 2D area than on a line; therefore, the probability of significant errors in the calculated elastic constants is larger.

In conclusion, we compared the values of  $\bar{C}_{ij}$  (1) calculated in [7] with our calculations of  $\tilde{C}_{ij}$  (6) obtained with the method of [6] for FM bcc Fe crystal. We used the full-potential linear muffin-tin orbital method (FPLMTO) [13], which performed well in our previous studies. The exchange–correlation functional in the form offered in [14] included the gradient corrections [15]. All relativistic effects were taken into account except spin–orbital couplings for valence electrons, which were treated in the scalar-relativistic approximation. Electrons in 3s, 3p, 3d and 4s states were treated as valence electrons, and semi-core states were not treated separately. The basis set was formed of orbitals of s, p, d, and f type. In the prism-shaped Brillouin zone a mesh for integration over  $\vec{k}$ -space with the linear tetrahedron method was constructed by dividing each edge into 50 parts ( $50 \times 50 \times 50$  mesh). Figures 1 and 2 show the calculated elastic moduli characterizing shear strains:  $\tilde{C}' = (\tilde{C}_{11} - \tilde{C}_{12})/2$  and  $\tilde{C}_{44}$ , respectively. A solid curve corresponds to our calculation, and a dashed curve presents the results from [7, 8]. In our calculations we thoroughly controlled the strain so that, on the one hand, it was large enough to allow the specific energy variation to exceed the calculation error



**Figure 2.** The elastic constant  $\tilde{C}_{44}$  for FM bcc Fe as a function of pressure. Solid circles—our results; open circles—results from [7, 8]. Experimental data: solid triangles—[16]; open triangles—[17]; open squares—[18]; solid squares—[19].

and, on the other hand, it was so small that no electronic topological transitions occurred under strain [20]. This condition determined the values of pressure at which the elastic constants were calculated.

We believe that the significant discrepancy between the curves in figures 1 and 2 resulted from the above discussed difficulties in ensuring acceptable accuracy, which are inherent to the method of determining the elastic constants proposed in [7]. This conclusion is proved by the experiment. According to our calculations, the conclusion drawn in [7] regarding the loss of mechanical stability by FM bcc Fe crystal under high pressure is valid; however, the value of pressure at which this structure loses stability appears to be two times higher.

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